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SEPARATORS FOR HIGH-RATE, NON-RESERVE ZINC-SILVER OXIDE BATTERIES

SEMIANNUAL REPORT

BY

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ASTROPOWER LABORATORY, DOUGLAS AIRCRAFT COMPANY
NEWPORT BEACH, CALIFORNIA

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ABSTRACT

This report covers the first half of a program on the investigation of separator materials for high rate, nonreserve zinc-silver oxide batteries capable of operation at temperatures as high as 165°F.

The films were obtained by blending an inorganic material (previously used to make separators for secondary silver-zinc cells) with an organic binder.

The program consisted of four tasks:

1. Characterization of Inorganic Materials

Two basic materials designated 3355-25 and 3420-09 were selected to make separators which were used as controls and were evaluated for resistivity, inertness in KOH at 77°F and at 165°F, silver and zinc diffusion rates and resistance to oxidation by silver saturated KOH solution. Although both materials showed close characteristics, the material 3420-09 was selected for its greater stability in KOH at 165°F.

2. Initial Composite Film Preparation and Characterization

For blending, two types of organic binders, K and P, and three procedures were used:

Procedure A: The film was cast on glass or Teflon.

Procedure B: A slurry was introduced in a porous thin matrix.

Procedure D: The silver electrode was dipped in the liquid formulation, resulting in a dip-coated electrode.

The results favored the binder P as more stable. The resistivities of the most promising films were in the range of 7 to 15 ohm-cm and the silver ion diffusion rates were lower than those obtained with the inorganic separators on the previous task.

3. Final Composite Film

This task in effect until the end of the program is aimed at continued improvement and evaluation of certain films selected from the previous task.

4. Cell Test and Evaluation

A few cells with dip-coated electrodes tested at room temperature maintained an OCV of 1.86 V after 31 days to date. A formal cell test program plan covering 72 cells is being started.

FOREWORD

The work described in this report was accomplished under Contract No. DAAB07-67-C-0310, DA Project No. 1C6 22001 A053-02-55. The work described here covers the first half of that to be completed. The authors would like to acknowledge the contribution of Messrs. F. C. Arrance and A. Rosa for the development and fabrication of separators; the assistance of Mr. G. Boehm, Mrs. L. Campagne and Mrs. R. Sheridan for carrying out the laboratory measurements and compilation of data; and Dr. S. K. Asunmaa for her electronmicroscopic investigation of separators.

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Section 1

SUMMARY AND CONCLUSIONS

This report covers the first half of a program on the investigation of separator materials for high rate, nonreserve zinc-silver oxide batteries capable of operation at temperatures as high as 165°F.

The program involves the use of inorganic separator materials developed at this laboratory over the past five years. Inorganic materials are blended with stable organic polymeric binders to form composite films. It is thereby possible to obtain thin films possessing the high ionic conductance of the inorganic granules and their high stability with the film-forming characteristics and stability of the organic binder.

The program plan consisted of four distinct tasks. The following is a detailed outline of significant results obtained during the current report period.

Task I: Characterization of Inorganic Materials

Two of the most promising inorganic materials, 3355-25 and 3420-09, were selected for this study and separators about 25 mils thick were made at different porosity levels.

(a) Both types manifested comparable resistivities in 31% KOH at 77°F in the range of 10 to 15 ohm-cm.

(b) The 3420-09 type separators were particularly stable at 77°F and at 165°F over the one-month test period.

(c) Silver diffusion rates appear to be unaffected by separator porosity at the low levels selected. On the other hand, zinc ion diffusion rates increased slightly with increased porosity.

(d) Resistance to oxidation by soluble silver species in KOH was good over the one-month test period. At 77°F, the amount of silver picked-up was negligible, whereas at 165°F it was in the range of 1 mg/in^2.

It was decided to employ the granulated 3420-09 inorganic material exclusively in the development of composite inorganic-organic films because of its more uniform behavior in the stability tests.

Task II: Initial Composite Film Preparation and Characterization

Different film compositions comprised of 3420-09 inorganic materials and one of two kinds of organic polymer binders K and P were prepared by the following three basic procedures:

Procedure A: The film is cast on glass or Teflon

Procedure B: A slurry is introduced in a porous thin matrix

Procedure D: The silver electrode is dipped in the liquid formulation, resulting in a dip-coated electrode.

The concentration of the inorganic component ranged from 75% to 95%. The films obtained were generally in the range of 5 to 10 mils.

(a) The resistivities of the most promising composite films in 31% KOH at 77°F were in the range of 7 to 15 ohm-cm.

(b) Dimensional stability tests indicated that films using binder P were particularly inert in KOH over the one-month test period, even at 165°F.

(c) Silver ion diffusion rates for the composite films were at least ten times lower than those obtained for the inorganic separators. Zinc ion diffusion rates were comparable.

(d) Resistance to oxidation by soluble silver species in KOH at 77°F and 165°F, determined by the amount of silver pick-up, was higher for the composite films than for the inorganic separators. However, the P binder composite films picked up less silver than K binder types.

At the end of this task, it was decided to further the development of composite films using exclusively type P binder, as prepared by procedures A, B and D.

Task III: Final Film Fabrication and Evaluation

This task in effect until the end of the program is aimed at continued improvement and evaluation of a formul n selected from the previous task and used to make films by procedures A, B and D with particular emphasis on the use of a small amount of plasticizer sufficiently inert under the test conditions. These films were constantly evaluated for resistivity, inertness in KOH, silver and zinc ion diffusion at 77°F and even at 165°F, and resistance to oxidation. A correlation was attempted between the silver ion diffusion rates obtained by three different methods.

Task IV: One Ampere-Hour Zinc-Silver Oxide Cell Tests and Evaluation

A few cell tests were performed, involving dip-coated silver electrodes, to establish any weak points in the cell fabrication techniques. It was soon discovered that the electrode edges were not adequately coated. When inert coating was applied around the edges, a considerable improvement in uniformity of results and longevity was achieved. To date,

ten cells have maintained an OCV of 1.85 to 1.86 V after 31 days at room temperature. A formal cell test program plan covering 72 cells is being started.

In summary, the feasibility of the approach has been demonstrated in the following manner:

(a) Composite films at the thickness level of 5 mils are readily obtainable.

(b) Their resistivity is in the range of 7 to 15 ohm-cm.

(c) They manifest good dimensional stability at temperatures as high as 165°F.

(d) Compared to the inorganic separators which have been used in secondary cells and have shown long cycling capability,* the silver ion diffusion rate is at least 10 times lower, the zinc ion diffusion rate is equivalent and the resistance to silver oxidation is slightly higher.

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*Arrance, F. C., Program to Develop an Inorganic Separator for a High Temperature Silver-Zinc Battery, Douglas Report SM-48461-F, Astropower Laboratory, Douglas Aircraft Company, Newport Beach, California, June 1967.

Section 2
INTRODUCTION

The principal problem with separators for high rate, nonreserve zinc-silver oxide batteries capable of operating at temperatures as high as 165°F is chemical instability. The reactive nature of the electrodic components, as well as the required use of caustic electrolyte, are the causes. Since 1962, this laboratory has been developing ceramic inorganic separators that are inert in severe environments while possessing low resistances.* These separators are prepared from synthetic as well as naturally occurring alkali-alkaline earth alumino silicates. The final product has a specific porous microstructure designed to permit the passage of hydroxyl ions while inhibiting the transfer of silver and zincate ions. Simultaneously, the ceramic bonds of the separator structure make it inert to attack by silver oxide.

To achieve some degree of flexibility and reduce the separator thickness to 5 mils, this laboratory has developed composite inorganic-organic separator systems as well. These systems are prepared as composites of inorganic components with inert organic polymeric binder. Since the inorganic component is present in at least 75% by weight, the essential beneficial aspects of this material are retained. The sole function of the organic component is to bond the inorganic material together.

The purpose of this program is to investigate separator materials for high rate, nonreserve zinc-silver oxide batteries for obtaining a readily producible film having the following properties:

1. Electrical Resistance — this is not to be above that of untreated PUDO-300 Cellophane (about 7-9 ohm-cm).
2. Inertness to Electrolyte — the separator should be unaltered by 31% aqueous KOH solution over long periods of time (three to five years) from -40°F to +165°F.
3. Impermeability to Ions — the separator should be impermeable to silver and zincate ions over the temperature range -40°F to +165°F. This property is considered to be not only a function of pore size but also polar and steric factors.

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*Berger, C., Arrance, F. C. and Taylor, A. D., Inorganic Separator for High Temperature Silver-Zinc Battery, NASA CR-54749, Douglas Report SM-46220-F, Astropower Laboratory, Douglas Aircraft Company, Newport Beach, California, September 1965.

*op. cit. Arrance, F. C.

4. Thickness — it is preferred that the thickness should not exceed 5 mils.

5. Resistance to Oxidation — the separator material should be resistant to oxidation by divalent s. ver oxide.

In order to derive the separator material best capable of meeting the above requirements, a program based on the following four tasks was initiated.

TASK I — Preparation and Characterization of Inorganic Materials

TASK II — Initial Film Preparation and Characterization

TASK III — Final Film Fabrication and Evaluation

TASK IV — One-Ampere Hour Zinc-Silver Oxide Cell Tests and Evaluation

The program is concerned with selecting an optimum inorganic material and the formulation of several inorganic-organic composites, accompanied by a series of evaluations designed to satisfy the requirements outlined above. Finally, the three most favorable systems will be subjected to actual cell tests to complete the evaluation.

This report provides a description of the results obtained during the first-half of the program. During this period, Tasks I and II have been completed and Tasks III and IV were in process. The results of Tasks I and II have led to the establishment of three basic film formulations which merited further pursuit under Task III and possibly Task IV.

Separator mechanistic interpretations, experimental procedures and results and the program plan for the second half are described in the sections which follow.

Section 3

THE MECHANISM OF SEPARATOR BEHAVIOR

These discussions apply to inorganic materials. To date, our understanding of separator behavior has been based on physical tests which have included microscopic observations. Optimum separator behavior in a nonreserve primary zinc-silver oxide cell exists when there is maximum resistance to the migration of silver and zincate ions on stand while, simultaneously during discharge, there is minimum resistance to the migration of hydroxyl ions from cathode to anode.

It was recognized early in the development of ceramic separators that lower resistivities of the order of 10-ohm-cm in 31% KOH at 77°F could be achieved. Microscopic analysis extending down to the ultra-fine structure indicates that total separator porosity was due to the following types of pores, listed in descending relative order of pore size.

1. crystallographic defects
2. intergrannular channels
3. intercrystalline channels
4. crystallographic (intracrystalline) channels.

From their more frequent, widespread occurence, it was evident that the major portion of the contribution to the overall separator porosity was that due to the intercrystalline and crystallographic channels where pore size is at the Angstrom level.

Therefore, it was evident that composite separators comprised of inorganic material at the micron particle size level with inert organic binder, the latter at a concentration $\leq 25\%$, could result in feasible films. By the start of the current program, some films of this type had been prepared and evaluated. It was found from resistivity data that our approach was valid.

Efforts on the mechanism of separator behavior are continuing. The lowest resistivity appears to be achieved when the migration of ions occurs through a liquid phase mechanism through the pores and channels of the separator matrix. The mechanism is aided by adsorption of solvent molecules on the sides of the pores. Such adsorption is governed by electrostatic as well as steric factors. Consequently, the conductance mechanism of separators is not governed by pore size alone. For example, it was demonstrated* during studies performed at this laboratory

*Strier, M. P. and Littman, F. E., Inorganic Separators for Nonaqueous Electrolyte Batteries, presented at the Spring Meeting of the Electrochemical Society, May 7-12, 1967, Dallas, Texas, Douglas Paper 4294.

in polar, nonaqueous media that an increase in separator resistivity occurred at higher temperatures. This was attributed to increased migrating ion collisions with the walls of the channels resulting from desorption of the solvent molecules from these walls.

Ideally, the function of the separator material is to permit the passage of hydroxyl ions while preventing the passage of silver and zincate ions. The separator material possessing the proper network of channels involving pore size, tortuosity and polar forces could accomplish this goal to a high degree. The large variety of inorganic compositions available coupled with the wide versatility of mechanical structures attainable from ceramic processing techniques are conducive to producing worthwhile ceramic structures. A number of ceramic compositions have been prepared here. Two of the most favorable systems, 3355-25 and 3420-09, were selected for initial screening tests constituting Task I of this program. The results of these tests should lead to selecting the better system for formulation into composites with organic binder; this will constitute the remainder of the program.

Section 4
WORK PERFORMED

4.1 TASK I: PREPARATION AND CHARACTERIZATION OF INORGANIC MATERIALS

The prime inorganic separator selected had the designation 3355-25 and 3420-09. They are fabricated from 100% inorganic materials (ceramic type) into square shapes of approximately 2" x 2" x 0.025". The objective was to characterize both types in terms of resistivity, inertness in KOH, impermeability to silver and zincate ions and resistance to oxidation in order to select one for incorporation in an inorganic-organic composition as called out by Task II.

Specifically, the tests applied were in order:

(a) determination of physical characteristics (dimensions, mass, porosity, transverse strength),

(b) electrical resistivity in 31% KOH at 77°F,

(c) inertness in KOH at 77°F and 165°F,

(d) silver and zincate diffusion rates at 77°F,

(e) silver pick-up at 77°F and 165°F, and

(f) microstructural analysis.

Because the changes noted at 77°F are insignificant and the extent of these changes decreases with decreasing temperature, measurements at very low temperatures (-40°F) were not considered useful.

Table I gives a list of the specific magnitudes measured or calculated, with their legend and their test conditions. The symbols will be consistently used throughout this report.

4.1.1 Physical Characteristics

For each inorganic material, 3355-25 and 3420-09, three and two levels of porosity, respectively, were selected. On each one, three sample pieces (approximately 2" x 2" x 0.025") were submitted to physical measurements to determine their dimensions, weight, water pick-up or water absorption (percent of dry weight), corresponding volume porosity (void percentage of total volume), and transverse strength.

The measurements were performed with calibrated calipers and analytical balances. The water absorption is done by soaking the specimen in water under vacuum at 29 inches Hg for one-half hour, blotting the surfaces dry and weighing.

TABLE I

DETERMINATION OF SEPARATOR CHARACTERISTICS BY MEASUREMENTS

1. Physical

Description	Unit	Dry	Water Wet
Thickness	mils	t	t'
Area	cm^2	A	A'
Volume	cm^3	V	V'
Mass	g	m	m'
Apparent Density	g/cm^3		$d_o = \frac{m}{V}$
Water Absorption	%		$a_o = \frac{m' - m}{m} \times 100$
Porosity	%		$p_o = \frac{m' - m}{V} \times 100$
Transverse Strength	psi		t. s.

2. Electrical:

Resistivity in 31% KOH

3. Inertness in KOH:

Measurement of dimensions and KOH wet mass after 7, 15, 30 days immersion in KOH at 77°F and 165°F.

4. Impermeability to Ions:

Silver diffusion rate: a (mg-mil/in^2-hour)
Zincate diffusion rate: b. 10^{-5} (moles-mil/in^2-minute)

5. Resistance to Oxidation:

Determined by silver pick-up c in mg/in^2 of separator material immersed in a silver ion saturated solution of 31% KOH at 77°F and 165°F over 30 days.

The same samples are dried to constant weight then used in the KOH immersion test (Paragraph 4.1.3).

Transverse strength measurements were performed by the equipment and procedure given in Appendix A.2. The measurements are performed on specimens 0.500 ± 0.001 inch wide. Samples are broken on the testing machine and the modulus of rupture is calculated as shown.

The averages and results are given in Table II.

4.1.2 Resistivity in KOH

The apparatus and procedure for determining resistivity under A.C. conditions is given in Appendix A.1. The separator samples were vacuum impregnated with 31% KOH solution by applying a vacuum of 29 inches Hg for 30 minutes. Generally, it was found that the sample was sufficiently wetted by this treatment for the resistivity to remain nearly constant over the first 24 hours of soaking.

The results of resistivity measurements are given in Table III where the averages are representative of at least three determinations with the average deviation being within ± 10%. It had become apparent during the course of dimensional stability tests on both types of ceramics that the 3420-09 material was more stable in 31% KOH solution. The 3420-09 samples were stored in 31% KOH solution under two kinds of thermal conditions. In one, the sample was kept at 77°F for 15 weeks; in the other, the samples were kept at 165°F for one month, followed by 11 weeks at 77°F. The changes in resistivity seem negligible, whereas greater changes occur for the 3355-25 samples which had been stored for much shorter periods of time.

4.1.3 Inertness in KOH

From a practical standpoint, it was decided to perform stability tests on samples in the following manner. At 77°F, three two-inch square samples were placed in polyethylene bottles with covers and kept immersed under 150 cc of 31% KOH solution. The work at 165°F was performed in sealed polysulfone cases in which three samples were kept immersed under 100 cc of 31% KOH solution. The following measurements on air-dried samples were made initially — area, thickness, weight and porosity (see Paragraph 4.1.1). The samples were then soaked in 31% KOH. Initial saturation with KOH was achieved by vacuum impregnation at 29 inches Hg. After the 7, 15 and 30-day immersion periods, measurements were made on the KOH wet test specimens. The results are summarized in Table IV.

The two different 3420-09 separators appear to manifest excellent dimensional stability during the one-month stand tests at both 77°F as well as

TABLE II

100% INORGANIC SEPARATORS
PHYSICAL CHARACTERISTICS – DRY

Material	Sample Designation	A cm^2	t mils	m (g)	a_o (%)	p_o (%)	t. s. (psi)
3355-25	I-AL-1	28.9	21	3.12 - 3.19	20.9	42.5	7,000
	I-AL-2	24.6	26	3.73 - 3.76	15.8	36.3	8,000
	I-AL-3	23.5	25	3.65 - 3.70	11.6	28.4	12,000
3420-09	I-OL-1	24.1	26	3.98 - 4.01	7.9	19.8	10,000
	I-OL-2	28.0	26	3.79 - 4.05	15.7	33.1	7,100

TABLE III

100% INORGANIC SEPARATORS RESISTIVITY IN 31% KOH

Material	Sample Designation	Original	After 15 Weeks at 77°F	After 4 weeks at 165°F and 11 weeks at 77°F
3355-25	I-AL-1	10.0 ohm-cm	NOT TESTED *	
	I-AL-2	13.0 ohm-cm		
	I-AL-3	15.1 ohm-cm		
3420-09	I-OL-1	30.9 ohm-cm	25.5 ohm-cm	24.7 ohm-cm
	I-OL-2	10.5 ohm-cm	9.8 ohm-cm	10.8 ohm-cm

* Degraded (See Table IV)

at 165°F. However, 3355-25 separators at the higher porosity ranges, I-AL-1 and I-AL-2, became too fragile before the end of the 30-day period to permit completion of their evaluation. The overall evaluation of Table IV appears to favor the I-OL series as more stable than the I-AL series.

4.1.4 Impermeability to Ions

A limited number of additional tests were performed on the samples, particularly the 3420-09 material for further correlative purposes. These tests, consisting of silver diffusion and zincate diffusion, had been specified for the inorganic-organic composites and will be described in greater detail in Section 4.2 and Appendix A. The results obtained for the Astroset materials are summarized in Table V.

1. Silver Diffusion

The apparatus, procedure and method of calculation are described in Appendix A. Measurements were performed over a six-hour period with readings of the amount of silver diffusion as ascertained by colorimetric analysis taken at two-hour intervals. There does not appear to be any correlation between silver diffusion rate and separator porosity, at the low porosity levels selected.

2. Zinc Diffusion

The apparatus, procedure and method of calculation are described in Appendix A. Measurements for the ceramic separator are performed over a 15-hour period. The higher porosity 3420-09 separators (I-OL-2) manifest higher zinc diffusion rates than the lower porosity 3420-09 separator (I-OL-1). However, the 3355-25 (I-AL-3) separator manifests a significantly higher zinc diffusion rate, while its porosity is actually lower than that of the I-OL-2 separators.

4.1.5 Resistance to Oxidation

The procedure for performing this at both 77°F and 165°F is given in Appendix A. Measurements were performed after one and two weeks and finally after one month exposure of the sample in 31% KOH solution saturated with silver oxide. The results given in Table VI indicate no significant differences between the two 3420-09 samples.

4.1.6 Microstructural Analysis

Electron micrographs of polished surfaces of a 3420-09 separator (I-OL-1) and a 3355-25 separator (I-AL-3) are shown in Figures 1 and 2, respectively. The grain size of the 3420-09 separator appears to be larger than that for the 3355-25 separator. In the electron micrograph of the

TABLE IV

100% INORGANIC SEPARATORS
INERTNESS IN 31% KOH (MEASUREMENTS DONE WET)

Material	Sample Designation	Days on Stand	77°F				165°F			
			A cm^2	t mils	m grams	p_o %	A cm^2	t mils	m grams	p_o %
3355-25	I-AL-1	0	28.9	21	3.96-4.04	42.1	28.9	21	3.86-4.02	40.1
		7	28.9	21	3.96-4.05	42.2	*		*	*
		15	28.9	21	3.95-4.04	41.9	*	*	*	*
		30	*	*	*	*	*	*	*	*
	I-AL-2	0	24.6	26	4.44-4.47	33.2	24.6	26	4.40-4.58	34.8
		7	24.6	26	4.50-4.53	36.1	24.6	26	4.39-4.56	33.7
		15	*	*	*	*	*	*	*	*
		30	*	*	*	*	*	*	*	*
	I-AL-3	0	23.5	25	4.25-4.33	31.6	23.6	25	4.24.4.44	32.9
		7	23.5	25	4.25.4.30	30.8	23.6	25	4.23-4.40	31.9
		15	23.6	25	4.23-4.29	30.5	23.6	25	4.18-4.34	29.1
		30	23.5	25	4.25-4.30	30.9	23.6	25	4.22-4.39	31.1
3420-09	I-OL-1	0	24.1	26	4.34-4.41	18.5	23.9	26	4.27-4.39	18.8
		7	24.1	26	4.38-4.44	20.0	23.9	26	4.27-4.41	19.2
		15	24.1	26	4.38-4.44	20.3	23.9	26	4.26-4.40	18.7
		30	24.1	26	4.38-4.44	20.0	23.9	26	4.28-4.42	19.6
	I-OL-2	0	28.0	26	4.58-4.87	33.1	28.0	26	4.73-4.81	34.1
		7	28.0	26	4.57-4.87	33.2	28.0	26	4.70-4.80	33.2
		15	28.0	26	4.57-4.87	33.1	28.0	26	4.68-4.78	32.4
		30	28.0	26	4.56-4.85	32.4	28.0	26	4.69-4.79	32.8

*Test discontinued; samples not suitable for further testing.

TABLE V

100% INORGANIC SEPARATORS IMPERMEABILITY TO IONS

Material	Sample Designation	Silver Diffusion mg-mil/in^2-hr. a (Average over 4 hours) Readings	Average	Zinc Diffusion, b x 10^{-5} moles-mils/in^2-min. b (Average over 15 hours Readings	Average
3355-25	I-AL-3	Not Tested *		10.6	
	(p = 28.4%)			11.3	11.0
3420-09	I-OL-1	0.31		1.65	
	(p = 19.8%)	0.25		2.33	
		0.15	0.24	1.33	1.77
	I-OL-2	0.24		6.75	
	(p = 33.1%)	0.24		3.28	5.02
		0.15			
		0.18	0.20		

*Findings on material degradation (Table IV) made tests unnecessary.

TABLE VI

100% INORGANIC SEPARATORS
RESISTANCE TO OXIDATION

Material	Sample Designation	Days on Stand	Ag Pick-up, c (mg/in^2) 77°F Readings	77°F Average	165°F Readings	165°F Average
3355-25	I-AL-3	7	0 0	0	0	0
		15	0 0	0	0.29 0.29	0.29
		30	0 0	0	0.87 0.86	0.86
3420-09	I-OL-1	7	0 0 0	0	0 0.57 0.86	0.48
		15	0 0	0	1.15 0.86	1.0
		30	0.14 0.14	0.14	1.69 1.71	1.70
	I-OL-2	7	0 0	0	0.72 0.72	0.72
		15	0 0	0	1.42 1.15	1.28
		30	0.12 0.12	0.12	1.71 1.47	1.59

Figure 1. Electron Micrograph of a Polished Surface of the Interior in Separator 3420-09. Magnification 11,000 X

Figure 2. Electron Micrograph of a Polished Surface of the Interior of Separator 3355-25. Magnification 11,000X

3355-25 sample, macropores are depicted as large channels between the sintered particles or polycrystalline grains. Several channels are pointed out by arrows. Micropores of crystallographic dimensions are shown under the arrows in the upper field of the electron micrograph in Figure 1. The size of the sintered grain varies between one and five microns. The channels may surround an entire grain, but show a maximum width of about one micron. They may even be larger in regions where three or four grains meet. A rich microporosity is also indicated on the channel surfaces.

In the electron micrograph of the 3420-09 separator (Figure 1), there is a more intricate, fine structure than for the 3355-25 separator. This means that the former has a higher percentage of micropores than the latter. The defect-rich structure of the 3420-09 material appears to cause a pronounced fine structure on the internal surfaces and shows a multitude of spacings above crystallographic dimensions. Overall, the 3355-25 material is characterized by larger intergranular channel spacings than those existing in the 3420-09 separator. This could account for the significantly higher zinc diffusion rates of the 3355-25 separator.

Concentrating on the 3420-09 material, photomicrographs of the surface studies of separator samples at 10% and 20% porosity, are shown in Figure 3. Note the large grain size and intermediate material of low reflectivity that is indicative of high porosity in the sample with 20% porosity. In the sample with 10%, there is significantly smaller grain size and a high light reflectivity over the entire surface. Photomicrographs of 3420-09 samples, depicting cross sections where the porosity is outlined through methylene blue staining are shown in Figures 4 and 5.

4.1.7 Inorganic Material for Film Formulation

The final selection of inorganic material for use in the composite formulation during the remainder of the program was based on overall performance of three samples of both types of materials. Because two of the three 3355-25 samples manifested some instability in 31% KOH solution during the 30-day stand period, it was decided to use the 3420-09 material. All of the 3420-09 samples showed excellent dimensional stability under these test conditions. One exception was noted in the silver degradation test at 165°F, i.e., the one surviving 3355-25 sample (I-AL-3) showed approximately one-half the amount of degradation manifested by the 3420-09 samples by the end of the 30-day period. However, the 3355-25 manifested significantly higher zincate diffusion rates and less favorable microstructural characteristics based on wider intergrannular channels and less well-defined fine structure.

Figure 3. Photomicrographs of Surface Structure in 3420-09 Separators With Estimated Porosity of 10 and 20% Respectively. Note large grain size and intermediate material of low reflectivity, that is indicative of high porosity in sample 20%. Note the significantly smaller grain size and a high light reflectivity over the entire surface in sample with 10% reported porosity. Magnification 450X

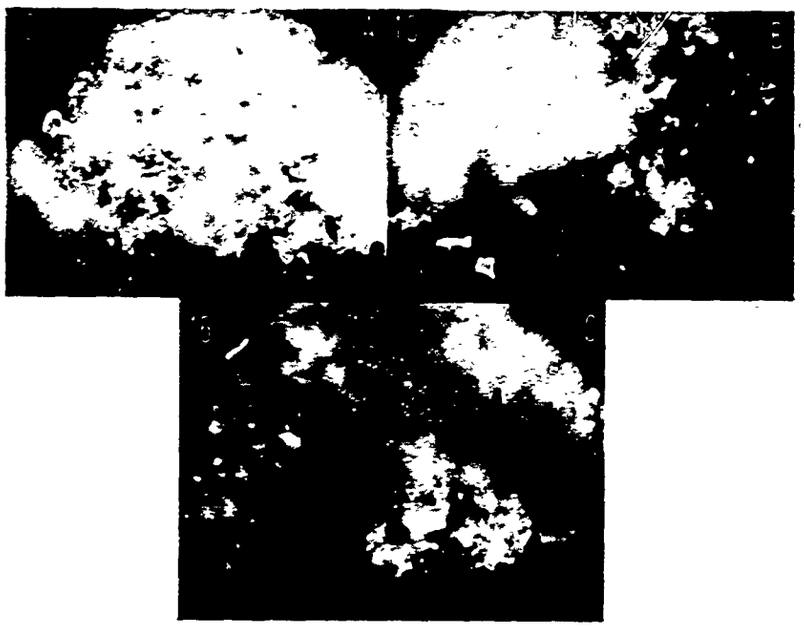

Figure 4. Photomicrographs (Reflected Light) Depict Methylene Blue Penetration Patterns on Separator Cross Sections. Fracture surfaces were examined, therefore certain regions only are well focused. Exterior surface of separators marked ee in each micrograph, penetration direction shown by arrow. The dark color displays blue stained regions. Note the low penetration in most areas (A) of sample 10%, an occasional high porosity region as in photomicrograph B. The path in B, exceptional in sample 10%, is more characteristic of sample 15% as shown in C. Magnification 450X

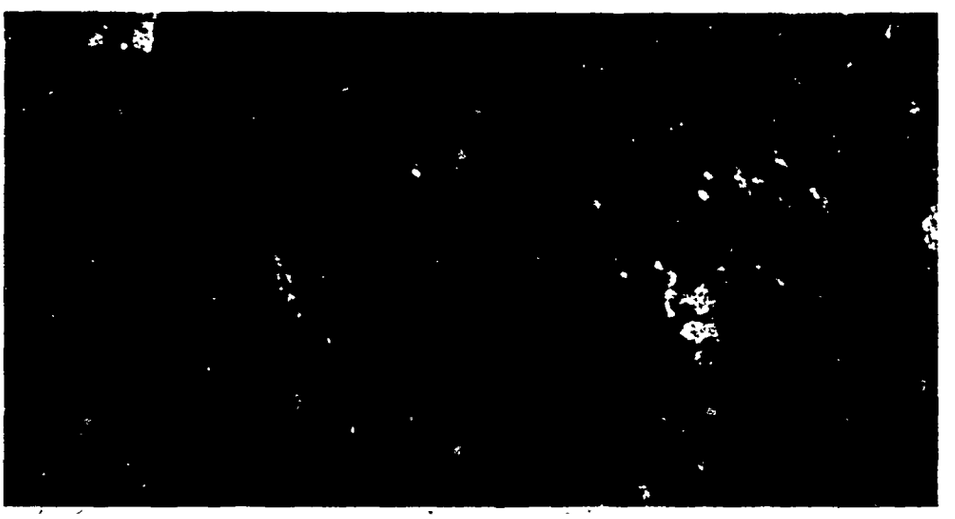

Figure 5. Photomicrographs of Methylene Blue Penetration in Individual Grains Showing Selected Staining. Certain crystallographic planes and defect regions are easily accessible to the stain molecules. Magnification 2,300X

4.2 TASK II – INITIAL FILM PREPARATION AND CHARACTERIZATION

The purpose of this task was to prepare and evaluate several composite formulations in order to be able to select the most promising system for more detailed study and optimization. The inorganic material selected from the results of Task I was the material coded 3420-09. In this task, two types of organic binders have been used, K and P, with minor modifications as to their grade and three different procedures have been employed in the preparation of composite film.

Procedure A: Membrane

The five essential steps involved are as follows:

Mixing

Casting

Curing

Drying

Post-treatment

The 3420-09 material was added with stirring to a solution of organic polymer binder and plasticizer (if necessary) in polar solvent. The latter was ground down to micron particle size. Then the homogeneous mixture was cast either on a glass or Teflon-coated plate. After air drying at 77°F, the film was cured at 350°F for 15 minutes. Occasionally, it was found expedient to release the film by soaking it in water.

Procedure B: Slurry in Matrix

The porous organic matrix is suspended in a slurry of 3420-09 material in polar solvent in which the organic binder has been dissolved. Next, the coated matrix is air-cured at 250°F for 15 minutes.

Procedure D: Dip Coated Electrodes

The procedure is the same as for Procedure B, except that an uncharged silver electrode is suspended in the inorganic material-organic binder-solvent mixture.

The evaluations were performed by methods and with equipment described in Section 4.1 and Appendix A.

The only significant screening tests possible for films prepared by Procedure D, other than actual zinc-silver oxide cell tests, would be silver diffusion cell tests, as described below in Section 4.2.3.

Table VII gives a list of all composite (inorganic-organic) film formulations and their physical appearance, which served as a rough screening. The resistivity test served also as a concurrent means for further screening. These two tests narrowed down the choice of formulations worth further investigation.

4.2.1 Resistivity

This measurement was performed with the equipment described in Appendix A. As indicated above in Section 4.1.2 for the inorganic materials, the samples were vacuum-impregnated with 31% KOH solution by applying a vacuum of 29 inches Hg for 30 minutes. The results obtained are summarized in Table VIII.

Measurements are given over longer periods when it was observed that initial readings tended to change with increasing soak time. In all instances, this change was characterized by a decrease in resistivity.

The most noteworthy conclusion that could be reached from these results is that sufficiently low resistance composite separators comprised of the subject materials are attainable. Although some of the composites manifested excessively high resistivities, i.e., A-OL-11, A-OL-12 and A-OL-13, they were subjected to further tests such as dimensional stability and silver and zincate diffusion, etc., in order to facilitate the chemical composition-properties correlation in this phase of the program.

4.2.2 Physical Characteristics and Inertness in KOH

The procedures are similar to those outlined above for the inorganic materials in Section 4.1.1. At 77°F, three 2-inch square samples were placed in polyethylene bottles with covers and kept immersed under 150 cc of 31% KOH solution. At 165°F, three 2-inch square samples were immersed under 100 cc of 31% KOH solution in each polysulfone case. The dry and wet measurements were performed initially and after 7, 15 and 30-day periods. Table IX gives their physical characteristics.

The results obtained in KOH at 77° and 165°F are summarized in Tables X and XI. Considering the results at both temperatures, all of the samples containing Type K binder, manifested evidence of instability. The condition was most severe at 165°F. The samples comprised of Type P organic binder, and the B-OL-1(F) and B-OL-2(F), generally manifested less instability than the Type K samples, especially at 165°F.

It could be concluded from these tests that samples based on Type P organic binder should be studied further in Task III of this program.

TABLE VII

COMPOSITE FILMS PREPARED BY EACH PROCEDURE (TASK II)

Film Designation	Inorganic 3420-09, %	Organic Binder % Type	Plasticizer % Type	Physical Appearance
Procedure A				
A-OL-1	75	25, K-B		Weak
A-OL-2	75	25, K-B		Weak
A-OL-3	75	25, K-B		Good
A-OL-4	90	10, K-A		Weak
A-OL-5	90	10, K-A		Good
A-OL-6	95	5, P		Weak
A-OL-7	90	10, K-B		Good
A-OL-8	90	10, K-A		Good
A-OL-9	80	20, P		Good
A-OL-10	80	10, P	10, D	Good
A-OL-11	75	25, K-B		Good
A-OL-12	80	20, K-B		Good
A-OL-13	85	15, K-B		Good
A-OL-14	85	15, P-C		Good
A-OL-15	80	20, P-C		Good
A-OL-16	90	10, P-C		Good
A-OL-17	80	10, P	10, E	Good
A-OL-18	90	7.5, P	2.5, E	Good
Procedure B				
B-OL-1(F)*	90	10, P-F		Good
B-OL-2(F)*	90	10, P-F		Good
Procedure D				
D-OL-1	90	5, P		Good
D-OL-2	80	20, P		Good
D-OL-3	85	15, P		Good
D-OL-4	90	10, K-B		Good
D-OL-5	90	10, K-A		Good

*Matrix F)

TABLE VIII

COMPOSITE FILMS
RESISTIVITY IN 31% KOH AT 77°F (TASK II)

Binder	Sample Identification	Average of 3 Samples (ohm-cm)
	Procedure A	
K	A-OL-1	23.0
K	A-OL-2	16.0
K	A-OL-3	31.9
		22.8 (after 1 week in KOH)
		10.8 (after 2 weeks in KOH)
K	A-OL-4	10.3
K	A-OL-5	13.0
P	A-OL-6	15.8
K	A-OL-7	27.1
K	A-OL-8	25.0
P	A-OL-9	486
		419 (after 8 days in KOH)
P	A-OL-10	497 (after 8 days in KOH)
K	A-OL-11	244 (after 15 days in KOH)
K	A-OL-12	212 (after 15 days in KOH)
K	A-OL-13	572
P	A-OL-14	145
		39.8 (after 6 days in KOH)
P	A-OL-15	23.3 (after 6 days in KOH)
P	A-OL-16	29.7 (after 6 days in KOH)
P	A-OL-17	21.4
P	A-OL-18	17.4
	Procedure B	
P	B-OL-1(F)	19.5
		6.5 (after 45 days in KOH)
P	B-OL-2(F)	3.5

TABLE IX

COMPOSITE FILMS
PHYSICAL CHARACTERISTICS – DRY (TASK II)

Binder	Sample Designation	A (cm^2)	t (mils)	m (g)	a_o (%)	p_o (%)
	Procedure A					
K	A-OL-3	24.0	8	0.45	81.7	64.4
K	A-OL-5	24.7	9	0.80	28.0	40.8
K	A-OL-7	25.8	6	0.60	0.5	0.7
K	A-OL-8	26.0	5	0.50	0.7	1.0
K	A-OL-11	26.0	4	0.41	0.2	0.3
K	A-OL-12	25.8	4	0.32	5.5	6.1
K	A-OL-13	25.6	2	0.17	5.0	6.1
P	A-OL-14	14.4	6	0.37	5.4	9.0
P	A-OL-15	26.2	7	0.71	15.6	23.9
P	A-OL-16	25.0	6	0.65	11.0	18.4
	Procedure B					
P	B-OL-1(F)	8.5	12	0.28	68.0	58.4
P	B-OL-2(F)	Material not dried.				

TABLE X

COMPOSITE FILM – PROCEDURE A
INERTNESS IN 31% KOH (MEASUREMENTS DONE WET)
(TASK II)

Binder	Sample Designation	Days on Stand	77°F				165°F			
			A (cm^2)	t (mils)	m (g)	po (%)	A (cm^2)	t (mils)	m (g)	po (%)
K	A-OL-3	0	23.7	8	0.72	41.2	25.0	6	0.26	66 7
		7	23.7	8	0.71	40.5	*	*	*	*
		15	23.7	8	0.71	40.0	*	*	*	*
K	A-OL-5	0	25.0	9	1.09	41.6	25.0	8	1.02	38 8
		7	25.1	9	1.06	36.4	*	*	*	*
K	A-OL-7	0	25.8	6	0.70	20.1	25.6	6	0.73	26 3
		7	25.8	6	0.73	26.0	*	*	*	*
		15	25.8	6	0.72	24.0	*	*	*	*
		30	25.8	6	0.75	29.8	*	*	*	*
K	A-OL-8	0	26.1	5	0.64	30.1	25.7	5	0.65	39.6
		7	26.0	5	0.64	31.7	*	*	*	*
		15	26.0	5	0.64	31.4	*	*	*	*
		30	26.0	5	0.64	32.7	*	*	*	*
K	A-OL-11	0	25.9	4	0.43	6.2	25.8	4	0.42	7 5
		7	25.9	4	0.44	10.0	25.8	4	0.43	8.9
		15	26.0	4	0.45	11.6	25.7	4	0 42	7 0
		30	26.0	4	0.45	11.5	*	*	*	*
K	A-OL-12	0	25.8	4	0.36	14.1	25.8	3	0 34	20 2
		7	25.8	4	0.36	13.1	25.7	3	0.33	19.6
		15	25.8	4	0.37	14.5	*	*	*	*
		30	25.8	4	0.36	12.8	*	*	*	*

(Continued)

TABLE X (Continued)

COMPOSITE FILM – PROCEDURE A
INERTNESS IN 31% KOH (MEASUREMENTS DONE WET)

Binder	Sample Designation	Days on Stand	77°F				165°F			
			A (cm^2)	t (mils)	m (g)	po (%)	A (cm^2)	t (mils)	m (g)	po (%)
K	A-OL-13	0	25.8	2	0.20	14.1	25.8	2	0.19	13.8
		7	25.8	2	0.20	18.2	*	*	*	*
		21	*	*	*	*	*	*	*	*
P	A-OL-14	0	14.5	6	0.46	31.3	25.7	6	0.78	28.4
		7	14.5	6	0.47	33.5	26.4	6	0.83	37.5
		21	14.6	6	0.48	33.8	27.7	6	0.88	40.4
		30	14.7	6	0.48	33.6	27.9	6	0.90	43.4
P	A-OL-15	0	26.4	7	0.91	32.3	26.3	6	0.85	35.3
		7	26.8	7	0.92	34.9	26.5	6	0.86	37.1
		15	26.9	7	0.93	35.2	27.0	6	0.87	39.0
		30	*	*	*	*	*		*	*
P	A-OL-16	0	25.4	6	0.75	19.8	26.1	7	0.85	19.6
		7	25.7	6	0.75	19.8	27.4	7	0.91	30.8
		15	26.0	6	0.77	22.3	31.2	7	1.00	40.0
		30	25.9	6	0.76	20.7	32.6	7	1.07	48.3

*Test discontinued: sample not suitable for further testing.

TABLE XI

COMPOSITE FILM – PROCEDURE B
INERTNESS IN 31% KOH (MEASUREMENTS DONE WET)
(TASK II)

Binder	Sample Designation	Days on Stand	77°F				165°F			
			A (cm^2)	t (mils)	m (g)	po (%)	A (cm^2)	t (mils)	m (g)	po (%)
P	B-OL-1(F)	0	8.6	11	0.35	24.0	18.4	11	0.83	24.3
		7	8.3	11	0.36	25.7	18.1	11	0.85	27.2
		15	8.4	11	0.36	27.1	18.2	11	0.86	30.8
		30	8.5	11	0.36	25.6	17.7	11	0.84	27.5
P	B-OL-2(F)	0	24.7	28	4.18	*	24.8	29	4.74	
		7	24.9	28	4.14	*	23.8	29	4.40	
		15	24.4	27	4.00	*	22.4	28	4.22	
		30	24.4	26	4.12	*	19.7	28	4.16	

*Not measured (samples were not originally dried).

4.2.3 Impermeability to Ions

These tests were performed concurrently with the dimensional stability tests. The procedures are given in Appendix A. The results obtained for films prepared by Procedures A and B are summarized in Table XII.

For Procedure D (dip coated electrodes), uncharged silver plates were used, of the following specifications:

Dimensions:	1.6" x 1.6" x 0.022"
Silver powder:	4.5 grams
Approximate nominal capacity at high rate:	1 Ah

After the dip-coating procedure was completed, the coated electrode was charged at 75 mA for 20 hours. Then, the coated electrode was thoroughly rinsed in distilled water and immersed in a polysulfone case and covered with 50 ml of 31% KOH solution. One-ml samples of solution were removed from the solution after 2, 4 and 6 hours and analyzed for silver by the colorimetric procedure given in Appendix A. The diffusion rates were calculated ordinarily for a period of six hours of operating time, unless the diffusion rates were extremely low, whereupon a longer period was necessary. The silver diffusion rates are listed in Table XIII.

The D-OL-4 and D-OL-5 formulations are essentially the same as that for the A-OL-7 and A-OL-8 films, respectively. The diffusion rate for the D-OL-4 film appears to be less than that of the A-OL-7 film. For the D-OL-5 film, the rate must be considered as equal to or less than the A-OL-8 films. The low diffusion rates manifested by the D-OL-1 and D-OL-2 films indicated that further study of films based on P-type organic binder prepared by this procedure was in order under Task III.

4.2.4 Resistance to Oxidation

Table XIV gives all data on films prepared by procedures A and B. Procedure D (dip coated electrodes) can be qualitatively evaluated in cell tests by the OCV retention capability on stand.

4.2.5 Discussion of Results

The results listed in Tables XII and XIII indicate that silver diffusion rates of composite films are significantly lower than those obtained for the 100% inorganic samples as listed in Table V. No conclusions can be reached about the comparison of zinc diffusion rates; generally, these rates are about the same for both types of material, although occasionally the values for the composite films are lower. However, the resistance to silver oxidation is higher for the composite film.

TABLE XII

COMPOSITE FILMS
IMPERMEABILITY TO IONS (TASK II)

Binder	Sample Designation	Silver Diffusion, a (mg-mil/in^2-hr)		Zincate Diffusion, b x 10^{-5} (moles-mil/in^2-min.)	
		Readings [a]	Average	Readings [b]	Average
	Procedure A				
K	A-OL-3	4-hr. period		NOT TESTED (1)	
		0.119 0.203	0.161		
K	A-OL-4	NOT TESTED (1)		4-hr. period	
				16.0	16.0
K	A-OL-7	4-hr. period		4-hr. period	
		0.144 0.072 0 072	0.090	6.02 4.80 2.33	4.38
K	A-OL-8	6-hr. period		4-hr. period	
		0.117 0.023 0.047 0.093 0.056	0.067	8.06 3.11 5.86 8.84	6.47
P	A-OL-9	NOT TESTED (2)		4-hr. period	
				0.53 0.94 0.16 0.14	0.44
P	A-OL-10	NOT TESTED (2)		4-hr. period	
				0.34 0.23 0.18 0.20 0.46	0.35

(1) Materials found not suitable for further testing.

(2) Tests eliminated because of high resistivity obtained (Table VIII).

(Continued)

TABLE XII (Continued)

COMPOSITE FILMS
IMPERMEABILITY TO IONS (TASK II)

Binder	Sample Designation	Silver Diffusion, a (mg-mil/in^2-hr) Readings [a]	Average	Zincate Diffusion, b x 10^{-5} (moles-mil/in^2-min.) Readings [b]	Average
	Procedure A (Cont'd)				
K	A-OL-11	6-hr. period		4-hr. period	
		0.020		0.15	
		0.094		0.38	
		0.094	0.064	0.29	0.31
		0.019		0.44	
		0.094		0.29	
K	A-OL-12	95-hr. period		4-hr. period	
		0.000		1.50	
		0.000		1.30	
		0.000	0.0	1.27	1.29
		0.000		1.20	
		0.000		1.19	
K	A-OL-13	4-hr. period		4-hr. period	
		0.000		0.91	
		0.004		0.18	
		0.007	0.020	0.36	0.45
		0.070		0.35	
				0.46	
P	A-OL-14	6-hr. period		4-hr. period	
		0.028		0.61	
		0.028	0.028	0.35	0.52
		0.028		0.61	
P	A-OL-15	24-hr. period		4-hr. period	
		0.000		2.11	
		0.000		2.34	
		0.000	0.0	2.05	1.99
		0.000		1.47	
		0.000			
	Procedure B				
P	B-OL-2(F)	24-hr. period		NOT TESTED	
		0.016	0.016	(Samples had pinholes)	

TABLE XIII

COMPOSITE FILMS – PROCEDURE D
(DIP COATED ELECTRODES)
SILVER DIFFUSION (TASK II)

Binder	Sample Designation	Silver Diffusion a (mg-mil/in^2-hour)		Comments
		Readings	Average	
P	D-OL-1	6-hr. period		
		0.006		
		0.023		
		0.028		
		0.011		
		0.011	0.016	
P	D-OL-2	26.5-hr. period		
		0.008		Longer time span for measurement required because of low diffusion rate
		0.008		
		0.005		
		0.005		
		0.008	0.007	
P	D-OL-3	2-hr. period		
		0.034		Relatively high rate; could be due to openings at edges.
		0.085		
		0.137		
		0.137		
K	D-OL-4	69.5-hr. period		
		0.007		Longer time span for measurement required because of low diffusion rate.
		0.005		
		0.013		
		0.007		
		0.003	0.007	
K	D-OL-5	6-hr. period		
		0.143		Lack of uniformity; could be due to openings at edges.
		0.000		
		0.000		
		0.036		
		0.000		

TABLE XIV

COMPOSITE FILMS
RESISTANCE TO OXIDATION (TASK II)

Binder	Sample Designation	Days on Stand	Silver Pick-up, c (mg/in^2) 77°F Readings	77°F Average	165°F Readings	165°F Average
	Procedure A					
K	A-OL-3	1	7.0	7.0	20.15	20.15
		2	14.0	14.0	44.0	44.0
K	A-OL-4	1			29.65	29.65
		4	4.77	4.77		
K	A-OL-7	7	5.30 5.30 5.30	5.30	5.30 5.30 5.30	5.30
		15	7.42 5.30	6.71	*	
		30	*		*	
K	A-OL-8	7	3.71 4.61 3.71	3.86	*	
		15	*		*	
P	A-OL-9	7	0 0 0	0	9.54 8.48 8.48	8.83
		15	1.06 1.06 1.06	1.06	13.78 13.78 11.66	13.07
		30	1.06 2.12 2.12	1.77	13.78 13.78 13.78	13.78
P	A-OL-10	7	2.12 2.12 2.12	2.12	13.78 14.84 14.84	14.49
		15	5.30 5.30 3.18	4.59	12.72 13.78 12.72	13.07

(Continued)

TABLE XIV (Continued)

COMPOSITE FILMS
RESISTANCE TO OXIDATION (TASK II)

Binder	Sample Designation	Days on Stand	Silver Pick-up, c (mg/in^2) 77°F Readings	77°F Average	165°F Readings	165°F Average
	Procedure A					
P	A-OL-10 (cont'd)	30	12.72 5.30 11.66	9.89	15.90 16.96 13.78	15.55
K	A-OL-11	7	3.18 3.18 3.18	3.18	10.60 10.60 12.72	11.31
		15	8.48 9.54 7.42	8.48	13.78 12.72 *	13.25
		30	14.84 14.84 15.90	15.19	12.72 14.84 *	13.78
K	A-OL-12	7	3.18 3.18 3.18	3.18	*	
		15	7.42 8.48 7.42	7.77	*	
		30	14.84 12.72 14.84	14.13	*	
K	A-OL-13	7	2.12 3.18 3.18	2.83	*	
		15	4.24 4.24 4.24	4.24	*	
		30	*		*	

(Continued)

TABLE XIV (Continued)

COMPOSITE FILMS
RESISTANCE TO OXIDATION (TASK II)

Binder	Sample Designation	Days on Stand	Silver Pick-up, c (mg/in²) 77°F Readings	77°F Average	165°F Readings	165°F Average
	Procedure A (Cont'd)					
P	A-OL-14	7	6.36 7.42	6.89	28.62 26.50	27.56
		15	11.66 12.72	12.19	23.32 23.32	23.32
		30	20.14 19.08	19.61	21.20 21.20	21.20
P	A-OL-15	7	13.78 13.78	13.78	36.04 36.04	36.04
		15	19.08 19.08	19.08	40.28 39.22	39.75
		30	23.32 22.26	22.79	30.74 33.92	32.33
P	A-OL-16	7	3.18 3.18	3.18	23.32 32.86	28.09
		15	4.24 4.77	4.51	20.14 26.50	23.32
		30	8.48 8.48	8.48	21.20 27.56	24.38
	Procedure B					
P	B-OL-2(F)	21	3.18 2.65	2.92	5.30 5.30	5.30
		28	4.24 3.71	3.98	7.42 7.42	7.42
		35	4.24 4.24	4.24	4.24 4.24	4.24

*Samples could not be handled.

The relative orders of silver diffusion rates and silver oxidation rates indicate that silver ions pass through the inorganic materials without any reaction. On the other hand, the composite films could be impeding the passage of silver ions by reduction of the silver. This is evidenced by discoloration of the composite separator during the silver diffusion test.

Referring to Table XII, it appears that the nature of the organic binder itself does not affect the silver or zincate diffusion rates. Since both types of experiments were performed over relatively short periods of time in 31% KOH solution at 77°F, the instability of the Type K component would not be revealed. However, the resistance-to-oxidation test showed that type P materials survived longer than the Type K materials at 165°F (Table XIV).

4.2.6 Comments and Conclusions

From all of the studies conducted under Task II, including both formulation and evaluation, it was quite evident that composite films of at least 80% inorganic material 3420-09 could be prepared with promising properties. During the early preparative efforts involving Type K organic binder, it was not certain whether the lack of stability in 31% KOH was due to the procedure itself, or to the binder. Actually, prior studies of the Type K binder itself had indicated greater stability in KOH solution at elevated temperatures. This was the reason for its selection in this investigation, initially. However, it was recognized that the specific Type K materials evaluated up to that point were in a highly oriented polymeric state. It was not known to what extent the morphological character of Type K binder contributed to such stability.

By the end of Task II, enough composite films had been prepared with Type K binder to indicate that it would not be sufficiently stable in 31% KOH solution at 165°F because of the nature of its morphological state under the preparative conditions involved. Correspondingly, Type P organic binder appears to be far more stable, regardless of its morphology and must be considered the candidate for further studies under Task III. However, further improvements in fabrication procedures may be required. This would include relatively small amounts of plasticizer.

The composite formulation used in the last two films (A-OL-17 and A-OL-18) appeared to be the point of convergence of the series of films made by Procedure A.

They will be fully evaluated under Task III, with minor modifications in ratios of inorganic material, organic binder and plasticizer.

Procedure B is still under investigation

In Procedure D (Dip coated electrodes), two formulations are emerging. The D-OL-1 formulation (on dip coated electrodes) corresponding to the A-OL-6 formulation (film made by Procedure A) appears to be ready for evaluation in cell tests as demonstrated in the screening cell tests described in Paragraph 4.4 of this report. The film cured in situ (on the substrate of the electrode itself) appears more promising than the film of the same composition made by Procedure A. Following this idea, the emerging composition of the series A-OL-17 may also have value on dip-coated electrodes (Procedure D) in cell tests.

4.3 TASK III – FINAL FILM PREPARATION AND EVALUATION

All of the results of the exploratory program pointed to the adoption of the composite film system based on Type 3420-09 inorganic material with Type P organic binder. Procedures A, B and D all showed promise. Now, it becomes a matter of further perfecting the development of the final films.

This phase of the program was initiated during the mid-point of this report period and is scheduled for the remainder of the program. The prepared films are constantly evaluated for resistivity, dimensional stability, silver and zincate diffusion and resistance to oxidation.

The formulations used and their designations are listed in Table XV. During this report period, films were prepared by Procedures A, B, and D. A blank run was made for the purpose of establishing the properties of the plasticizer material.

4.3.1 Resistivity at 77°F

The summary of results is given in Table XVI. All films with the 3420-09 component have low resistivities. It was established from the stability studies described below that the decrease in resistivity with time is more film soaking phenomenon rather than due to film degradation.

4.3.2 Inertness in KOH

The results obtained at 77° and 165°F are summarized in Table XVII. All of the samples tested appear to be maintaining good integrity up to this point. The rather large changes in apparent porosity noted for B-OL-3(F) are due to the difficulty in drying the sample; this is characteristic of its particular mode of fabrication. Overall, the stability advantages observed in the Type P binder are borne out further at this point.

4.3.3 Impermeability to Ions

The tests were performed according to the procedures indicated above for the Task II films. Additional silver and zincate diffusion tests were performed at 165°F. The higher temperature diffusion tests were

TABLE XV

COMPOSITE FILMS PREPARED BY EACH PROCEDURE (TASK III)

Film Designation	Matrix	Inorganic Content %	Organic Binder		Plasticizer		Physical Appearance
			%	Type	%	Type	
Procedure A							
Blank		0	50	P	50	E	Good
A-OL-17		80	10	P	10	E	Good
A-OL-18		90	7.5	P	2.5	E	Good
Procedure B							
B-OL-3(F)	F	90	10	P	0		Good
B-OL-4(N)	N	80	10	P	10	E	Good
B-OL-5(W)	W	80	10	P	10	E	Good

TABLE XVI

COMPOSITE FILMS
RESISTIVITY IN 31% KOH AT 77°F (TASK III)

Sample Identification	Average of 3 Samples (ohm-cm)
Procedure A	
A-OL-17-1*	21.4
	7.8 (after 8 days in KOH)
A-OL-17-2*	17.4
A-OL-18	14.8
	10.4 (after 8 days in KOH)
Procedure B	
B-OL-3(F)	4.4
B-OL-4(N)	13.5
B-OL-5(W)	41.5

*These are 2 different batches of the same formulation A-OL-17

TABLE XVII

COMPOSITE FILMS
INERTNESS IN 31% KOH (TASK III)
(MEASUREMENTS DONE WET)

Sample Designation	Days on Stand	77°F				165°F			
		A (cm^2)	t (mils)	m (g)	p_o (%)	A (cm^2)	t (mils)	m (g)	p_o (%)
Procedure A									
Blank	0	25.9	2	0.11	—	25.9	1	0.09	—
	7	25.4	2	0.13	—	23.9	1	0.09	—
	15	25.3	2	0.12	—	23.8	1	0.09	—
	30	To be performed				To be performed			
A-OL-17-1	0	26.0	5	0.69	26.8	26.1	5	0.69	29.9
	0	26.0	5	0.69	26.7	25.8	5	0.69	32.4
	15	26.0	5	0.69	27.4	25.8	5	0.71	32.5
	30	26.0	5	0.69	26.3	26.3	5	0.69	32.5
A-OL-17-2	0	26.0	2	0.25	26.6	25.8	2	0.25	30.4
	7	26.0	2	0.25	26.4	25.7	2	0.25	30.2
	15	25.9	2	0.26	33.2	25.6	2	0.25	27.5
	30	25.9	2	0.25	26.2	25.6	2	0.23	19.7
A-OL-18	0	25.9	8	1.07	27.1	25.3	8	1.07	28.3
	7	25.9	8	1.08	27.9	25.3	8	1.11	34.0
	15	26.0	8	1.07	27.3	25.4	8	1.11	33.4
	30	26.0	8	1.08	28.4	25.5	8	1.11	33.0
Procedure B									
B-OL-3(F)	0	24.1	24	2.94	60.1	23.8	24	2.91	64.1
	7	19.9	24	2.20	26.2	19.2	24	2.40	46.0
	15	19.9	24	2.21	26.3	19.1	24	2.46	50.8
	30	19.9	24	2.22	27.5	19.1	24	2.51	53.2

performed with the same diffusion apparatus as described for the lower temperature work.

The results obtained are summarized in Table XVIII. As observed for the Task II films, the silver diffusion rates for the composite films are at 10 times lower than those for inorganic separators. It is to be noted from the limited tests at 165°F that there was an increase in the silver diffusion rate to about the level of that noted at 77°F for the inorganic separators. This is still a relatively low rate, since inorganic separators by themselves perform well in secondary cells over significant periods of time at temperatures as high as 212°F. *

As had been noted above for the Task II composite films, the zincate diffusion rates of the composite films are generally the same as those for the inorganic separators. It is of interest to note that the zincate diffusion rates do not appear to change with increasing temperature.

Measurements of silver diffusion rates through separators in the cylindrical diffusion apparatus have already been described (films made by Procedures A and B). In addition, the measurements of silver diffusion rates through coatings of silver electrodes (Procedure D) were described in Section 4.2.3. In order to establish a correlation between the two methods, a third method for performing this measurement was initiated. This consisted of wrapping one layer of composite film around a charged silver electrode. This electrode had the same specifications (dimensions, weight and charge) as given above for Procedure D film evaluations (Paragraph 4.2.3). After the charging was completed, the electrode was thoroughly rinsed with distilled water and dried at 65°C for two hours. After the composite film separator was wrapped around the electrode, the assembly was placed in a polysulfone case and immersed under 50 ml of 31% KOH solution. The procedures for measurement of silver diffusion rates was as described above for the dip-coated electrodes.

The results obtained are summarized in Table XIX. Included are the silver diffusion rates obtained for the same films in the cylindrical diffusion apparatus as reported above in Tables XII and XVIII and for the dip-coated electrodes of equivalent composition, as reported in Table XIII. Task II films are included for correlative purposes.

For the A-OL-7 film, the rates are lower for the dip-coated and wrapped electrodes than in the cylindrical cell. The extremely low silver diffusion rate for A-OL-15 film is equally evident from the cylindrical diffusion cell and wrapped electrode measurements. The rates for the A-OL-17 and B-OL-3(F) films by these methods are about the same.

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*op. cit. Arrance, F. C.

TABLE XVIII

COMPOSITE FILMS
IMPERMEABILITY TO IONS (TASK III)

Sample Designation	Silver Diffusion, a (mg-mil/in^2-hr)				Zincate Diffusion, b x 10^{-5} (moles-mil/in^2-min.)			
	a				b			
	77°F		165°F		77°F		165°F	
	Readings for 6-hr. Period	Average	Readings for 6-hr. Period	Average	Readings for 4-hr. Period	Average	Readings for 4-hr. Period	Average
Procedure A								
A-OL-17-1	0.028 0.000 0.027 0.147 0.000	0.040	0.051 0.058 0.058 0.058 0.089	0.063	4.00 3.77 3.95 3.95 3.44	3.82	1.71 1.77 1.73 1.90 2.24	1.87
A-OL-17-2	0.014 0.009 0.009 0.009 0.014	0.011	0.137 0.197 0.169	0.168	5.00 4.84 5.11 4.70 7.56	5.44		
A-OL-18	0.032 0.032 0.032 0.000 0.000	0.019	0.115 0.136	0.126	4.30 3.52 4.55 5.17 4.09	4.33	4.24	4.24
Procedure B								
B-OL-3(F)	0.138 0.125 0.085 0.098 0.175	0.124	0.064 0.054 0.056 0.000	0.044	10.8 9.6 14.9 16.6 12.2	12.8	14.3 11.2 12.7 12.6	12.7

TABLE XIX

COMPARISON OF SILVER DIFFUSION RATES OF COMPOSITE SEPARATORS BY THREE DIFFERENT PROCEDURES (TASK III)

(mg-mil/hr-in^2)

Film Designation	Diffusion Apparatus		Wrapped Electrodes		Dipped Electrodes		
	Readings	Average	Readings	Average	Corresponding Film Designation	Readings	Average
Procedure A							
A-OL-7	4-hr. period		125.5-hr. period		D-OL-4	69.5-hr. period	
	0.144 0.072 0.072 0.072	0.090	0.005 0.005	0.005		0.007 0.005 0.013 0.007 0.003	0.007
A-OL-8	6-hr. period				D-OL-5	6-hr. period	
	0.023 0.047 0.117 0.056 0.096	0.068	-- --			0.143 0.000 0.000 0.036 0.000	0.036
A-OL-15	6-hr. period		6-hr. period				
	0.000 0.000 0.000 0.000 0.000	0.000	0.000 0.000 0.000 0.042	0.011			
A-OL-17-1	6-hr. period		6-hr. period				
	0.028 0.000 0.027 0.147 0.000	0.040	0.000 0.000 0.026 0.022 0.063	0.022			

(Continued)

TABLE XIX (Continued)

COMPARISON OF SILVER DIFFUSION RATES OF COMPOSITE SEPARATORS BY THREE DIFFERENT PROCEDURES (TASK III)

(mg-mil/hr-in^2)

Film Designation	Diffusion Apparatus		Wrapped Electrodes		Dipped Electrodes		
	Readings	Average	Readings	Average	Corresponding Film Designation	Readings	Average
Procedure A (Cont'd)							
A-OL-17-2	6-hr. period		6-hr. period				
	0.014 0.009 0.009 0.009 0.014	0.011	0.311 0.142	0.227		NOT TESTED YET	
A-OL-18	6-hr. period		6-hr. period				
	0.032 0.032 0.032 0.000 0.000	0.019	0.202 0.098	0.150		NOT TESTED YET	
Procedure B							
B-OL-3(F)	6-hr. period		6-hr. period				
	0.138 0.125 0.085 0.096 0.175	0.124	0.222 0.122 0.219	0.188			

4.3.4 Resistance to Silver Oxidation

The results of the silver oxidation tests (Table XX) which could be considered the most severe and revealing indicate that the plasticizer E (blank run) must not be contributing to instability. A film capable of withstanding silver oxidation to the degree achieved by the 100% inorganic separators could be considered suitable. In this regard, the B-OL-3(F) film fulfills this requirement best. However, the A-OL series films are not out of range. The difference between the two A-OL-17 batches may be due to variations in the fabrication technique.

4.4 TASK IV – ONE AMPERE HOUR ZINC-SILVER OXIDE CELL TESTS

The purpose of this phase of the program is to determine separator performance in actual cell tests according to a formal, detailed testing program.

4.4.1 Preliminary Tests (22 Cells)

Prior to the initiation of the formal program itself, three series of preliminary cell tests have been performed (Table XXI) at 77°F.

Series No. 1

This series was concerned with the one ampere-hour zinc-silver oxide cell tests. The D-OL-3 (Table VII) formulation was used with silver plates having the dimensions described above in Section 4.2.3. The cells, comprised of one dip-coated silver electrode sandwiched between two counter zinc electrodes, were vacuum filled with 31% KOH solution. Then they were charged to 2.1 volt cut-off.

The results obtained are summarized in Table XXI. The initial capacity, Q_o, and plateau voltage, V_p, are based on the initial discharged at the 2C rate (2A). The cells have the rated capacity initially and the voltage plateau ranges from 1.16 to 1.28 volts. However, premature failures, as manifested by decrease of OCV below 1.84 V, were evident. Examination of cell components revealed that the edges of the silver electrode were inadequately coated, sometimes presenting bare areas.

Series No. 2

This was the same as Series No. 1, except that the D-OL-1 formulation (Table XII) was used in the coating of the silver electrode. The results obtained are summarized in Table XXI. The initial discharge voltage plateaus are uniformly at 1.36 V. It appeared that when the edges were fully protected as in Cells 2.2 and 2.6, that long wet stand life is possible.

TABLE XX

COMPOSITE FILMS
RESISTANCE TO OXIDATION (TASK III)

Sample Designation	Days on Stand	Silver Pick-up, c (mg/in^2)			
		77°F		165°F	
		Readings	Average	Readings	Average
Procedure A					
Blank	7	—	—	2.12 2.12 3.18	2.47
	15	2.12 1.06 1.06	1.14	1.06 2.12 3.18	2.12
	30	1.06 2.12 3.36	2.18	4.48 4.48 5.30	4.75
A-OL-17-1	7	3.18 3.18 2.12	2.18	20.14 16.96 18.02	18.37
	15	2.12 2.12 2.12	2.12	21.02 22.26 22.26	21.91
	30	7.42 6.36 6.36	6.71	21.20 23.32 22.26	22.26
A-OL-17-2	15	0.00 1.06 1.06	0.71	6.36 5.30 5.30	5.65
	21	1.06 1.06 1.06	1.06	6.36 6.36 8.48	7.07
	30	2.12 1.06 1.06	1.41	9.54 7.42 —	8.48

(Continued)

TABLE XX (Continued)

COMPOSITE FILMS
RESISTANCE TO OXIDATION (TASK III)

Sample Designation	Days on Stand	Silver Pick-up, c (mg/in^2)			
		77°F		165°F	
		Readings	Average	Readings	Average
Procedure A (Cont'd)					
A-OL-18	7	1.06 1.06 1.06	1.06	4.24 5.30 5.30	4.95
	15	1.06 1.06 1.06	1.06	6.36 6.36 6.36	6.36
	30	1.06 1.06 1.06	1.06	8.48 8.48 9.54	8.83
Procedure B					
B-OL-3(F)	7	0.00 0.00 0.00	0.00	2.12 2.12 2.12	2.12
	15	1.06 1.06 1.06	1.06	2.12 3.18 3.18	2.83
	30	1.59 1.06 1.06	1.24	3.71 3.71 4.24	3.89

TABLE XXI

SCREENING TESTS FOR PREPARATIVE DEFECTS IN DIP COATED ELECTRODES (TOTAL OF 22 CELLS)

Test	Cell Number	Capacity Q_6 (Ah)	Plateau Voltage Vp at 2A	Wet Stand Days (OCV ≥ 1.84 V)	Remarks
#1	1.1	1.1	1.22	2	Electrode edges unprotected
	1.2	1.1	1.23	1	
	1.3	1.1	1.28	1	
	1.4	1.0	1.20	8	
	1.5	0.8	1.16	16	
	1.6	1.0	1.26	1	
#2	2.1	1.0	1.36	Opened for Examination	
	2.2	1.1	1.36	44	
	2.3	1.2	1.36	1	Electrode edges unprotected
	2.4	1.1	1.36	12	
	2.5	1.2	1.36	13	
	2.6	1.1	1.36	50*	
#3	3.1	1.3	1.23	31* ⊗	All edges protected
	3.2	1.2	1.23	31* ⊗	
	3.3	1.3	1.29	31* ⊗	
	3.4	1.3	1.23	31*	
	3.5	1.3	1.27	31*	
	3.6	1.3	1.23	31*	
	3.7	1.3	1.22	31*	
	3.8	1.3	1.28	31*	
	3.9	1.3	1.31	31*	
	3.10	1.3	1.23	31*	
	⊗ Discharged after 31 days				
	3.1	1.3	1.22		
	3.2	1.0	1.17		
	3.3	1.2	1.19		
	Then recharged and put back on stand.				

*Tests still in progress.

Series No. 3

This series involves the same D-OL-1 formulation as in Series No. 2, except that all of the edges were systematically protected with inert compound. The inert compound was applied as a frame around the electrode. The results given in Table III indicated that all of the cells under test have maintained an OCV of 1.85 to 1.86 after 31 days. Three cells were discharged at the 2C rate (2A) after this stand time and then recharged and put back on stand. This series will be used mainly for checking OCV retention capability for the duration of the program.

4.4.2 Formal Cell Test Program (72 Cells)

At this point, this program is about to be started. Table XXII shows the test program plan as to procedure of fabrication of separators and assembly of cells and cell distribution for each variation. The test schedule and the breakdown of cell tests is as follows: A total of 72 cells will be built and divided into groups of three to be tested monthly over three months, at two temperatures for four combinations of two procedures, B and D, and two assembly techniques (dip or bag). The specific tests will be:

(a) Wet stand for 3 months (remainder of program).

(b) Group of 3 cells to be discharged at the end of each month (total of 9 cells).

(c) Group of 9 cells to stand at each temperature (77°F and 165°F) (total of 18 cells).

(d) Group of 18 cells for each variation (total of 72 cells).

(e) All other cells left from first series to continue tests to accumulate data on wet stand longer than 3 months.

TABLE XXII

TEST PROGRAM PLAN

Assembly of Cells

Dip Coating or Bagging Electrodes

Procedure	Code
Slurry of Inorganic Into Matrix (Bag)	B
Coating Silver Electrodes (Dip)	D

Formulation

Method	Inorganic 3420-09	Binder P	Plasticizer E	Procedure	Cell Assembly
1.	95%	5%	0%	D	Dip
2.	80%	10%	10%	D	Dip
3.	80%	10%	10%	B	Bag
4.	80%	10%	10%	D B	Dip Ag Bag Zn

Cell Distribution (72 Cells)

Method	Procedure \ Assembly	Dip	Bag
1.	D	18	
2.	D	18	
3.	B		18
4.	D & B	18	

Section 5
WORK PLANNED

The second half of the program will be concerned with the completion of Task III and Task IV.

5.1 PLAN FOR REMAINDER OF TASK III

5.1.1 Nature of Films to be Prepared by Procedure A

Emphasis will be on the continued use of binder P with plasticizer E. The effect of concentration of plasticizer over the range of 1-10% will be more firmly established.

5.1.2 Nature of Films to be Prepared by Procedure B

A procedure has been used to prepare films 5-mils thick with included matrix. The matrix will be formulated with the same 3420-09 organic binder-plasticizer formulations developed by Procedure A. Evaluation will be the same as in Section 5.1.1.

5.1.3 Nature of Films to be Prepared by Procedure D

Silver electrodes will be coated mainly with Procedure A formulations. Special attention will continue to be given to the edge effect. The coated electrodes will be evaluated for silver diffusion at 77°F and 165°F by the methods given in this report.

5.2 PLAN FOR THE REMAINDER OF TASK IV

The program plan as outlined in Table XXII will be executed. However, additions may be made as promising developments occur in Task III.

Appendix A

METHODS FOR BATTERY SEPARATOR MEASUREMENTS

A. 1 RESISTIVITY

This measurement is performed according to the method of Salkind and Kelly.* An AC method is used. The set-up is shown in Figure A-1. The sample is vacuum impregnated for at least 30 minutes in 31% KOH.

The voltage drop across two fixed platinized platinum electrode tips is measured. The resistance is first obtained for the electrolyte from the measurement of voltages at various currents. Voltage is plotted against current, the slope of the line gives the resistance R_e.

Then, the separator sample is inserted and the voltage-current relationship is determined, giving an overall resistance R_s. The resistance of the separator R is then:

$$R = R_s - R_e$$

The resistivity of the separator ρ in ohm-cm is then:

$$\rho = \frac{Ra}{t}$$

where a is the cross-sectional area of the active separator in cm^2 and t is the separator thickness in cm.

A. 2 TRANSVERSE STRENGTH OF INORGANIC SEPARATORS

Samples are broken on the transverse testing machine shown in Figure A-2. The modulus of rupture was calculated according to the equation:

$$M = \frac{3Pl}{2bd^2}$$

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*Salkind, A. J. and J. J. Kelly, Electrical Resistance-Alternating Current Method. Characteristics of Separators for Alkaline Silver Secondary Batteries. Edited by J. E. Cooper and A. Fleisher, Air Force Aero Propulsion Laboratory, p. 69.

where,

M = modulus of rupture (psi)

P = breaking load (pounds)

b = breadth (inches)

l = span (inches)

d = thickness (inches)

Tested specimens have the following measurements:

b = 1/2 inch

l = 1 inch

Formula used:

$$M = \frac{3P}{d^2}$$

A. 3 SILVER DIFFUSION

The measurement of separator impermeability to silver ions in 31% KOH solution is performed in the Lucite diffusion apparatus shown in Figure A-3. After the separator is vacuum impregnated at 29 inches Hg with 31% KOH solution for at least one half hour, it is installed in the diffusion apparatus between rubber gaskets as shown in Figure A-3. Both halves of the apparatus are bolted together. The primary side (100 ml volume) is filled with a saturated solution of silver oxide in 31% KOH solution. Then, the secondary side (50 ml volume) is filled with 31% KOH solution. Charged dipped electrodes are just placed in 50 ml of 31% KOH.

At two-hour intervals, a one-ml sample is pipetted from the secondary compartment and is analyzed for silver by the following colorimetric analysis.

A 1-ml sample is placed in a 25-ml volumetric flask to which 5.0 ml of 1.65 N nitric acid has been added. Distilled water is added to bring the level up to just below the neck of the flask (23-24 ml); then 1.0 ml of 0.05% rhodanine solution is added. Finally, it is filled up to the mark with distilled water.

A Klett-Summerson Photoelectric Colorimeter is used in the analysis. The colorimeter sample tube in rinsed twice with approximately 5 ml of the above sample before being filled with 10 ml of the sample for the absorption measurement. Before each absorption reading, the colorimeter is zeroed with a blank solution of the rhodanine in 31% KOH. The concentration of the silver ions is read directly from a calibration curve.

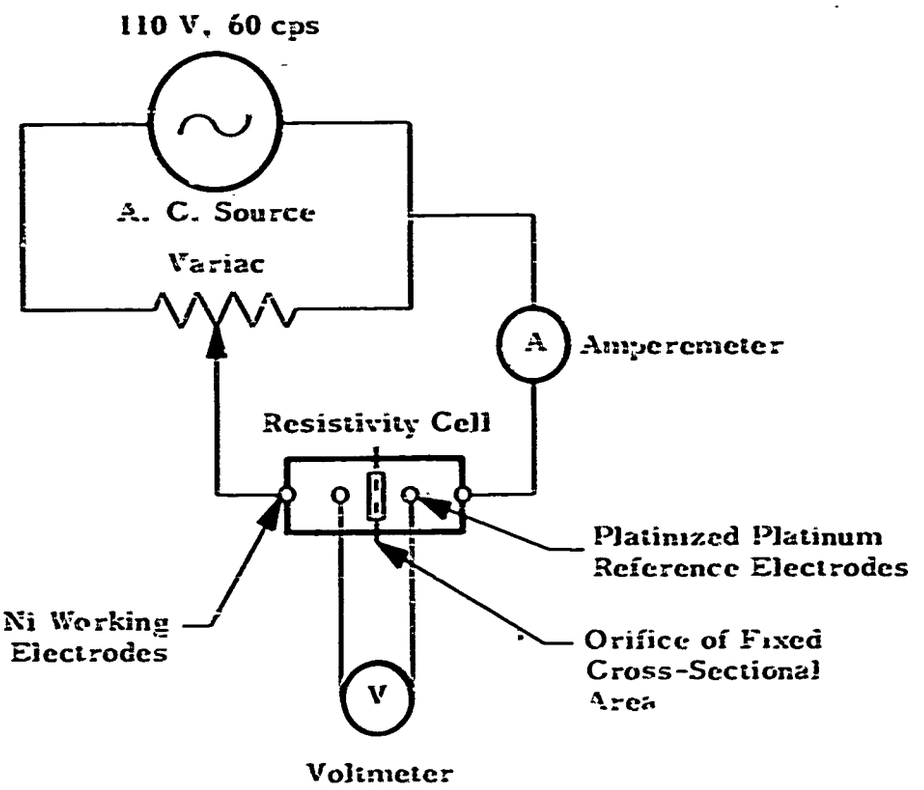
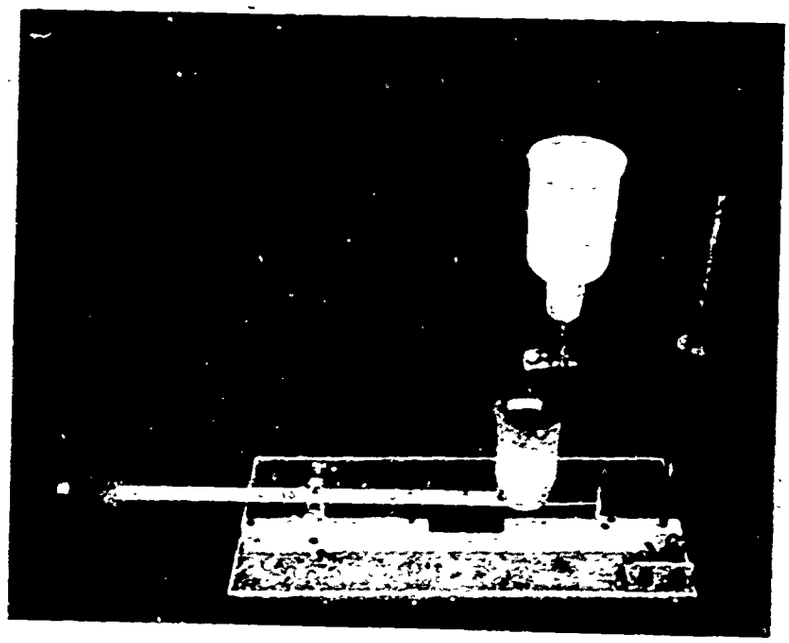


Figure A-1. Schematic of Resistivity Measuring Apparatus



C1136

Figure A-2. Transverse Strength Apparatus

Generally, readings were taken after two, four, and six hours and the rate was calculated over the six-hour period. For relatively rapid diffusion rates, the rates were calculated over two or four hours. For extremely low rates of diffusion, the experiment was performed over a longer period.

The average variation of concentration per hour is noted $G = \frac{\Delta C}{\Delta T}$ (mg/l)/hr. The rate of silver diffusion is the amount diffusing per hour through one square inch of separator one mil thick.

$$a = \frac{G \cdot t \times 50}{1000\ A} \qquad (\text{mg - mil/in}^2\text{-hr})$$

where,

t = thickness of separator in mils

A = area of separator in in^2 ($1.77\ in^2$)

A. 4 ZINCATE DIFFUSION

The diffusion apparatus is the same as that described for silver diffusion (see also Figure A-3), except that the volume of the secondary compartment is 100 ml. The following procedure was used: *

The separator sample is vacuum impregnated at 29 inches Hg with 31% KOH solution for 30 minutes. Then the sample is assembled with the diffusion cell. A stirring bar is placed in the secondary side and 1.0 ml of 0.1 M $ZnO_2^{=}$ in 31% KOH solution is added. Then, the secondary side is filled with 31% KOH solution and an amalgamated zinc strip and Hg-HgO reference electrode is inserted. A constant voltage power source is connected in opposition with the reference electrode. The tip of an argon purge tube is placed through the hole in the top of the diffusion apparatus close to the zinc strip, but above the solution.

The rich-zinc side of the apparatus is filled with saturated zincate solution of 31% KOH. The solution on the secondary side is stirred.

After 30 minutes, a reading of the difference in potential is made between the reference electrode and the partially immersed zinc strip. The measurement is repeated every 60 minutes over a period of four hours.

The concentration of zincate ion is obtained from a calibration curve giving correspondence of concentration and voltages.

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*Lander, J. J., Zinc Diffusion, ibid, p. 115.

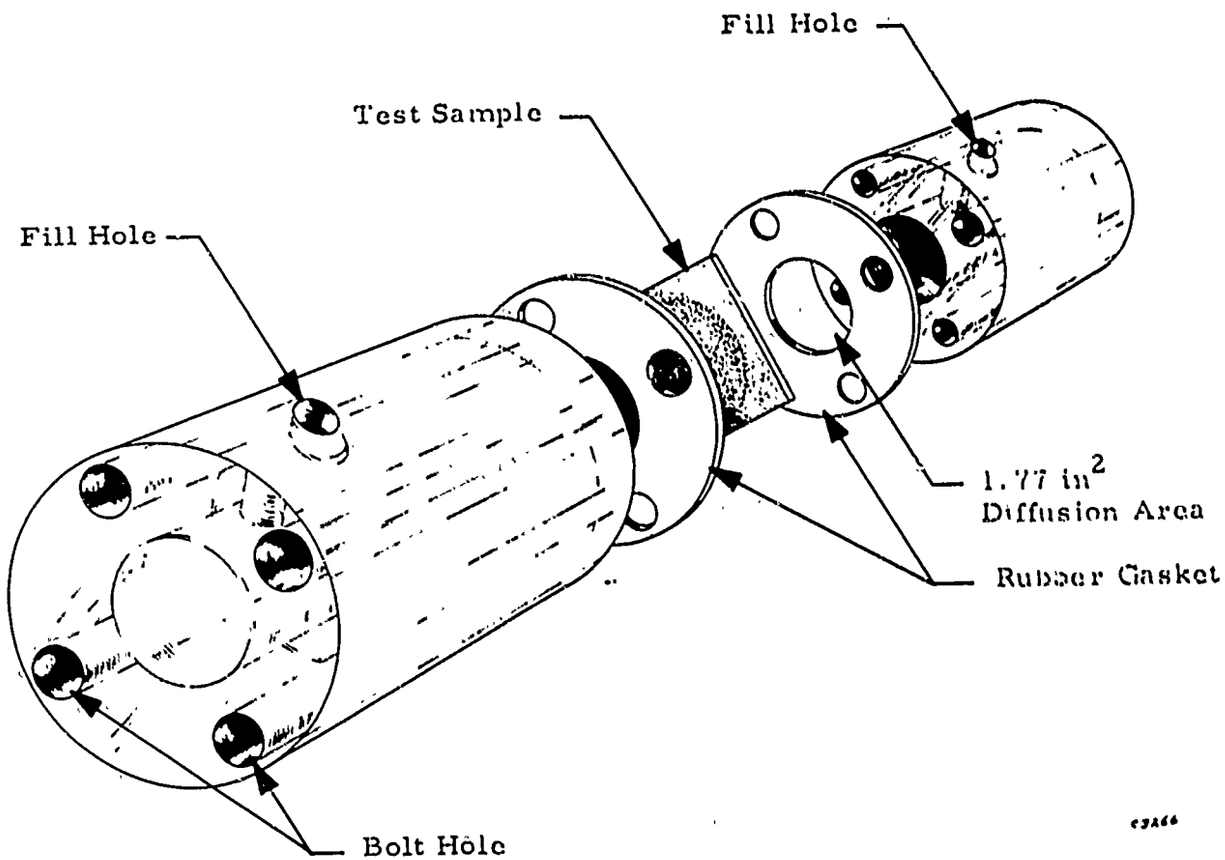

Figure A-3. Silver and Zinc Diffusion Apparatus

The average variation of concentration per hour is noted $G = \frac{\Delta C}{\Delta T}$ in (moles/l)/ minute.

The rate of zincate diffusion is the amount of diffusion per minute through one square inch of separator one mil thick.

$$b' = b.10^{-5} = \frac{G.t \times 100}{1000 \times A} \quad \text{(in moles-mil/in}^2\text{-minute)}$$

where,

t = thickness of separator in mils

A = area of separator in in^2 (1.77 in^2)

In order to simplify the tables, the factor b is given in the course of the report.

A. 5 SILVER PICK-UP*

Samples of one square inch cross-sectional area are suspended in a saturated solution of silver oxide in 31% KOH solution. The samples at 77°F are kept in stoppered polyethylene bottles. The tests at 165°F are kept in polysulfone cases. The volume of electrolyte used is 50 ml. After the requisite stand time, the sample is removed, washed several times with distilled water until neutral, and placed in a beaker containing 25 ml of 1:2 nitric acid. The sample is heated gently for one-half hour. Then 5 ml of ferric ammonium indicator is added and the sample is titrated with 0.1 N KCNS to a rust colored end-point. The amount of silver pick-up is determined in mg/in^2.

*Lander, J. J., Degradation of Soluble Silver, ibid, p. 77.

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Fort Monmouth, New Jersey 07703
AMSEL-KL-PD

13. ABSTRACT

[illegible]

The [illegible] were [illegible] and [illegible] separators for [illegible] [illegible] with [illegible] [illegible].

The program [illegible] [illegible].

1. [illegible]

[illegible] used as controls and were [illegible] [illegible] rates, resistance [illegible] the material [illegible] [illegible].

2. [illegible]

[illegible] were used.

Procedure A: [illegible] glass [illegible].

Procedure B: [illegible] the matrix.

Procedure C: [illegible] the liquid formulation, resulting in a [illegible] electrode.

The results [illegible] were more stable. [illegible] of the most promising films were in the range [illegible] were lower than those obtained for the [illegible] separators [illegible].

3. [illegible]

[illegible] of certain films [illegible].

4. [illegible]

[illegible] electrodes tested at room temperature maintained an OCV [illegible] after 21 days to date. [illegible] program [illegible] has been started.

DD FORM 1473

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Energy Storage						
Batteries						
Separators						
Electrochemistry						
Alkaline Cells						
Inorganic Materials						

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